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Interactions of PDMS with a surface.

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• Reinforcement of PDMS with filler particles leads to increased strength.

Q. What is the nature of the local reinforcement mechanism ?

A. Hooking between polymers adsorbed on the filler surface and the surrounding matrix.

The probability distribution for a single flexible chain is:

$$
\begin{aligned}
G_0(1,2;n) &\equiv \langle 1,n| \left[\partial_n - \left(\frac{b^2}{6}\right)\nabla^2\right]^{-1} |2,0\rangle \\
&\sim \int_{\vec{R}_2}^{\vec{R}_1} \mathcal{D}\vec{R}(n') \exp - \left[\left(\frac{3}{2b^2}\right)\int_0^n dn' \left(\frac{\partial \vec{R}(n')}{\partial n'}^2\right)\right] \\
&\sim \left(\frac{2\pi n b^2}{3}\right)^{-3/2} \exp - \left[\frac{3(\vec{R}_1 - \vec{R}_2)^2}{2nb^2}\right] \qquad (1)
\end{aligned}
$$

- where $\partial_n \equiv \frac{\partial}{\partial n}$.
- This expression is obtained by considering only the entropy of a flexible chain.

Alternatively,

$$\langle 1, n| \left[\partial_n - \left(\frac{b^2}{6}\right)\nabla^2\right]^{-1} |2, 0\rangle \sim$$

$$\int \mathcal{D}^2\psi\, \psi^*(\vec{R}_1, n)\psi(\vec{R}_2, 0) \exp -[\beta\mathcal{F}]$$

$$\beta\mathcal{F} = \int dn' d^3x\, \psi^*(\vec{x}, n') \left[\partial_{n'} - \left(\frac{b^2}{6}\right)\nabla^2\right] \psi(\vec{x}, n') \quad (2)$$

• Thus we have another way of thinking about a system of flexible polymers, in terms of $\psi(\vec{x}, n)$ and an energy functional $\beta\mathcal{F}$ which is isomorphic to one that describes diffusion.

• $(\vec{x}, n)$ labels the location $\vec{x}$ in physical space, of the n-th segment of a chain, and $|\psi(\vec{x}, n)|^2$ is the probability of finding a polymer segment at a given location in space.

• This is a density functional theory in the style of Kohn and Sham.

• Contains a description of *many* independent polymers. Hence more powerful than the single chain approach.

Density Functional formalism for *interacting* polymers

$$\mathcal{Z} = \int \mathcal{D}^2\psi \ \exp -[\beta\mathcal{F}] \ [\textbf{Partition Function}]$$

$$\beta\mathcal{F} = \int dn d^3x \, \psi^*(\vec{x},n) \left[\partial_n + H_0 + V\right] \psi(\vec{x},n)$$

$$V = \frac{v}{2}|\psi(\vec{x},n)|^2 - \mu$$

$$H_0 \equiv -\left(\frac{b^2}{6}\right)\nabla^2 \tag{3}$$

Extremizing the functional yields a Schrodinger-like equation (Hartree-Fock-like approximation):

$$\left[\frac{\partial}{\partial n} - \left(\frac{b^2}{6}\right)\nabla^2 - \mu_0 + v_{eff}|\psi(\vec{x},n)|^2\right]\psi(\vec{x},n) = 0 \qquad (4)$$

- $v_{eff} = v - w$, $1/2w$ is the probability per unit volume for cross-linking.

• Theory can be used to re-evaluate the basic physics of polymer melts, encapsulated in Flory's theorem:

At very low concentrations, fluctuations in the melt are high, but at high concentrations, they are so suppressed that the polymers begin to behave independently again.

• Can show that $R_g \sim N^\nu$, $\nu \approx 0.631$, for $c_0 \to 0$.

• Can show for $c_0 \to 0$, chains take on the appearance of a pearl necklace.

• Can show that the transition to entanglement is also a critical phenomenon, such that $R_g \sim (N^{-1} - 2\mu^{-1})^{-\nu}$.

• A tube model can be recovered for higher concentrations.

Surface Interactions

• Assume that adsorption occurs in a non-preferential manner, so that all segments of a polymer are equally likely to become attached to the surface. Take $\psi(\vec{r}, n) \equiv f(z)$:

$$\frac{d^2 f(z)}{dz^2} + f(z) - f^3(z) = 0 \tag{5}$$

where the length scale is $a = b/\sqrt{6c_0 v_{eff}}$ and the field has been scaled by $1/\sqrt{c_0}$, c_0 being the monomer number density.

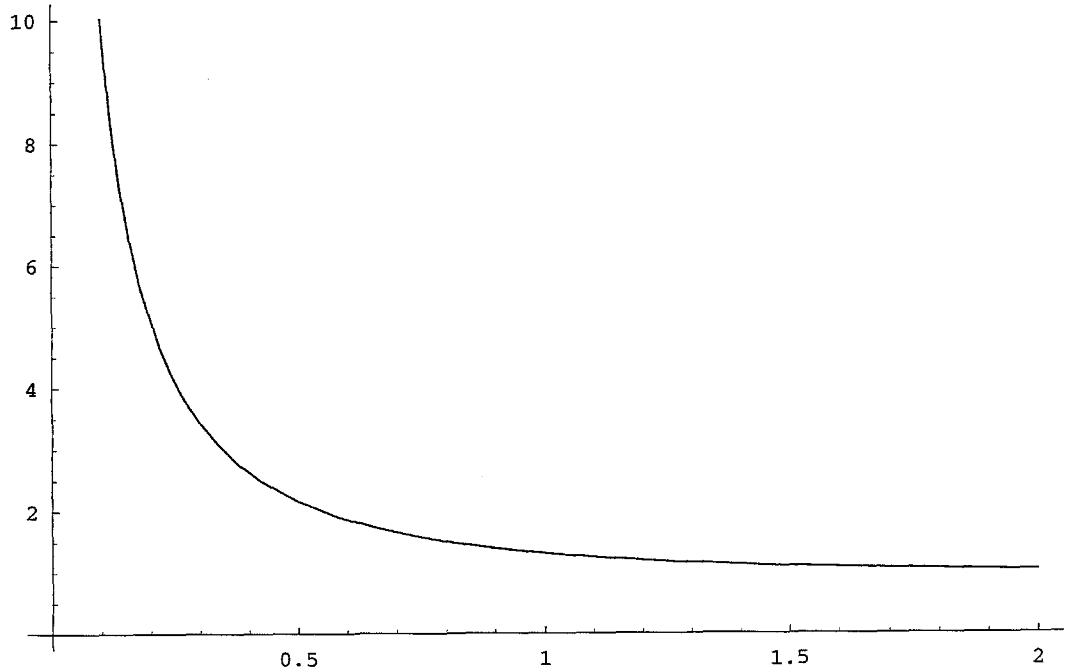
- Two solutions possible:

$$\begin{aligned} f_t(z) &= \coth\left(\frac{z-z_t}{\sqrt{2}}\right) \text{ [\textbf{Total}]} \\ f_m(z) &= \tanh\left(\frac{z-z_m}{\sqrt{2}}\right) \text{ [\textbf{Matrix}]} \end{aligned} \tag{6}$$

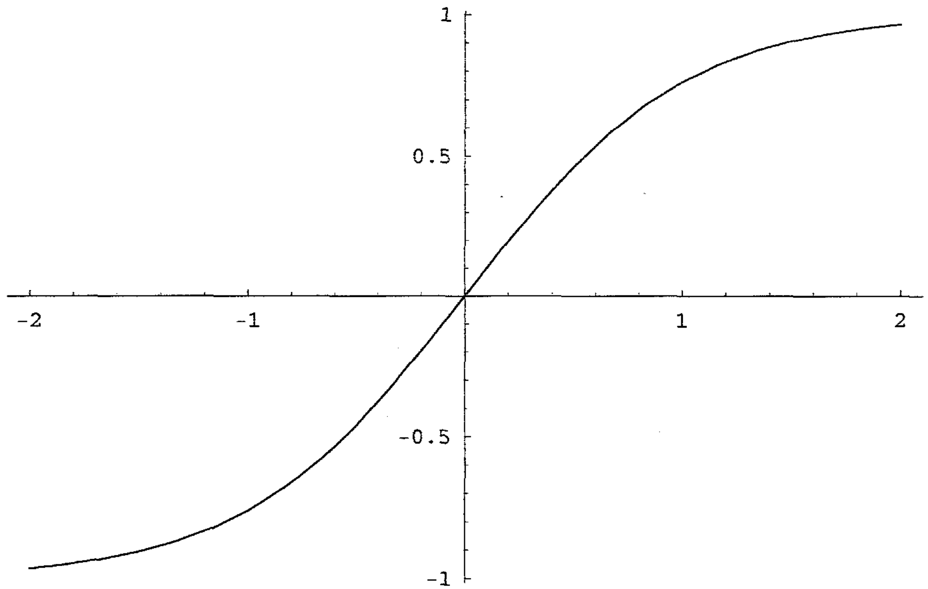
- Boundary condition:

$$-\left(\frac{d\ \ln f_t(z)}{dz}\right)_{z=0} = \lambda^{-1} \tag{7}$$

Coth function



Tanh function



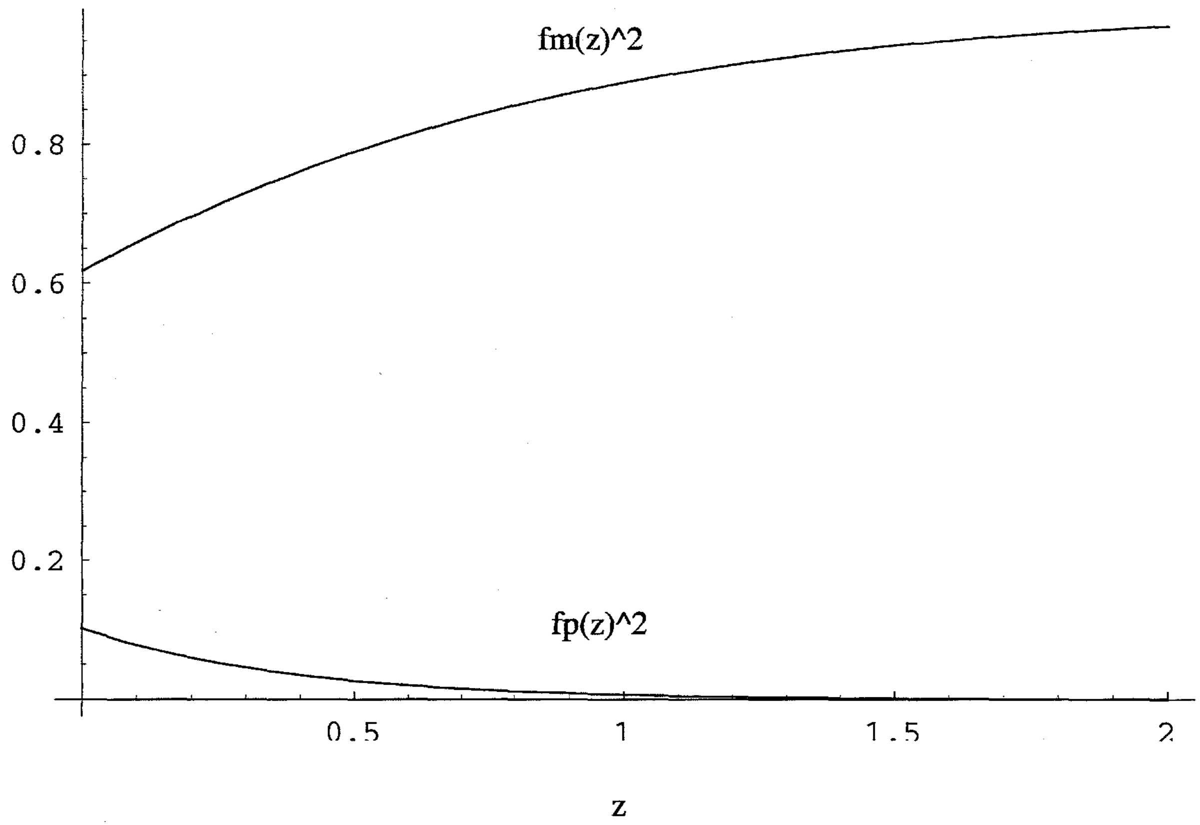
The profile of the pseudo-brush is given by the square of the following function:

$$f_p(z) = \coth\left(\frac{z - z_t(\lambda)}{\sqrt{2}}\right) - \tanh\left(\frac{z - z_m(\lambda)}{\sqrt{2}}\right) \tag{8}$$

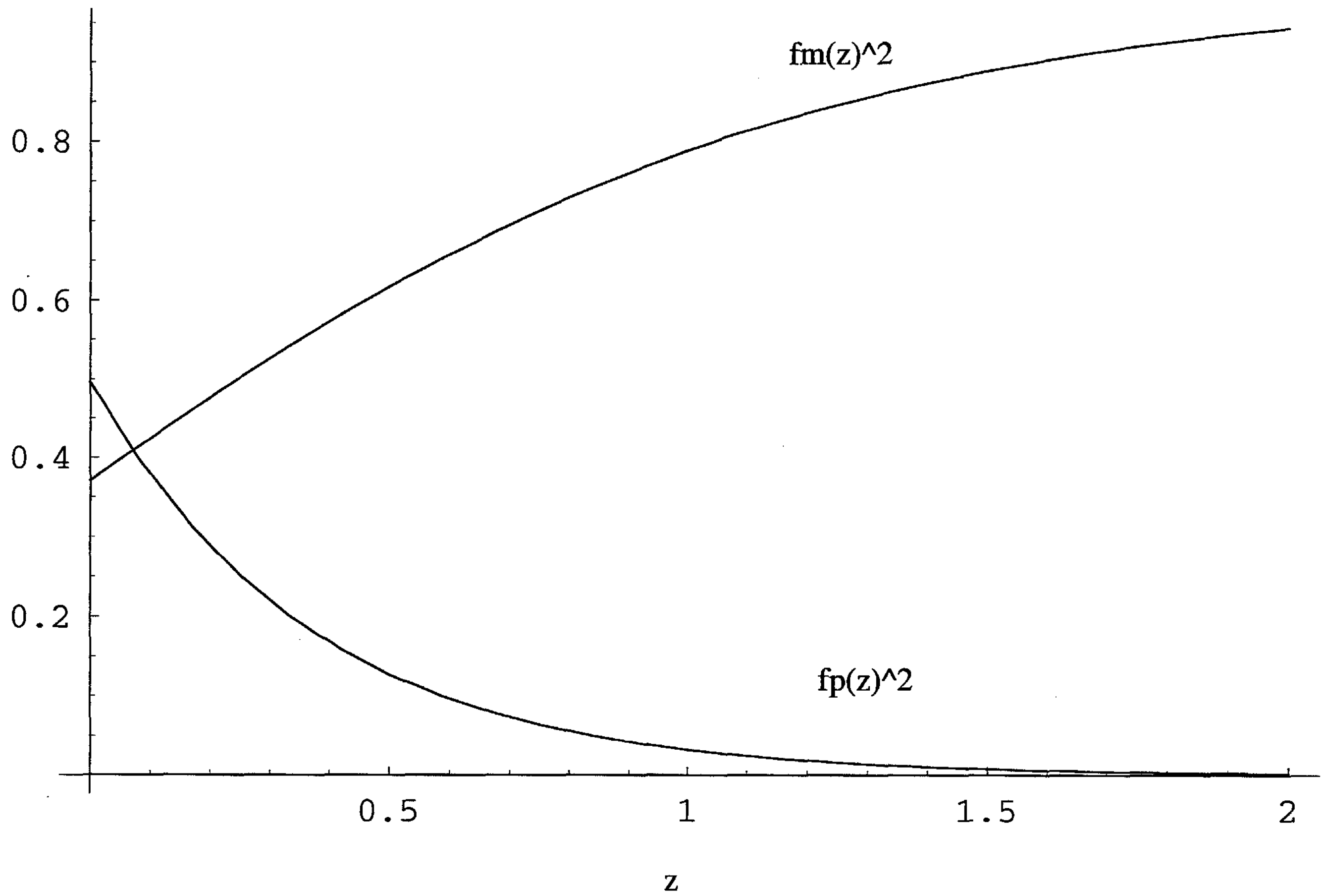
- Grafting density:

$$\frac{\sigma}{b^2} = c_0 \lambda a \left|f_p(z=0)\right|^2 \tag{9}$$

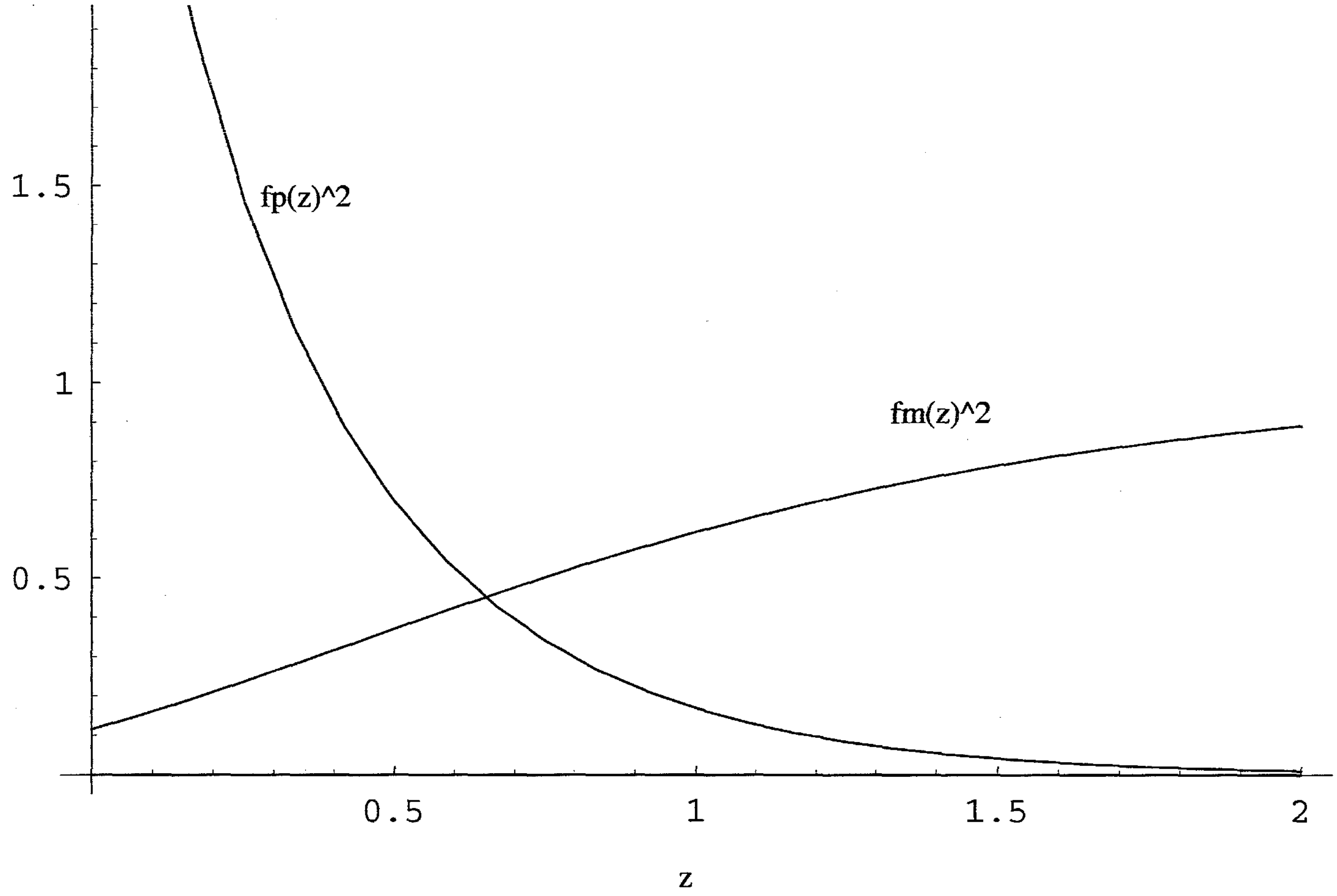
$\lambda = 1.5$ (weak adsorption)



$\lambda = 1.0$ (near optimal adsorption)



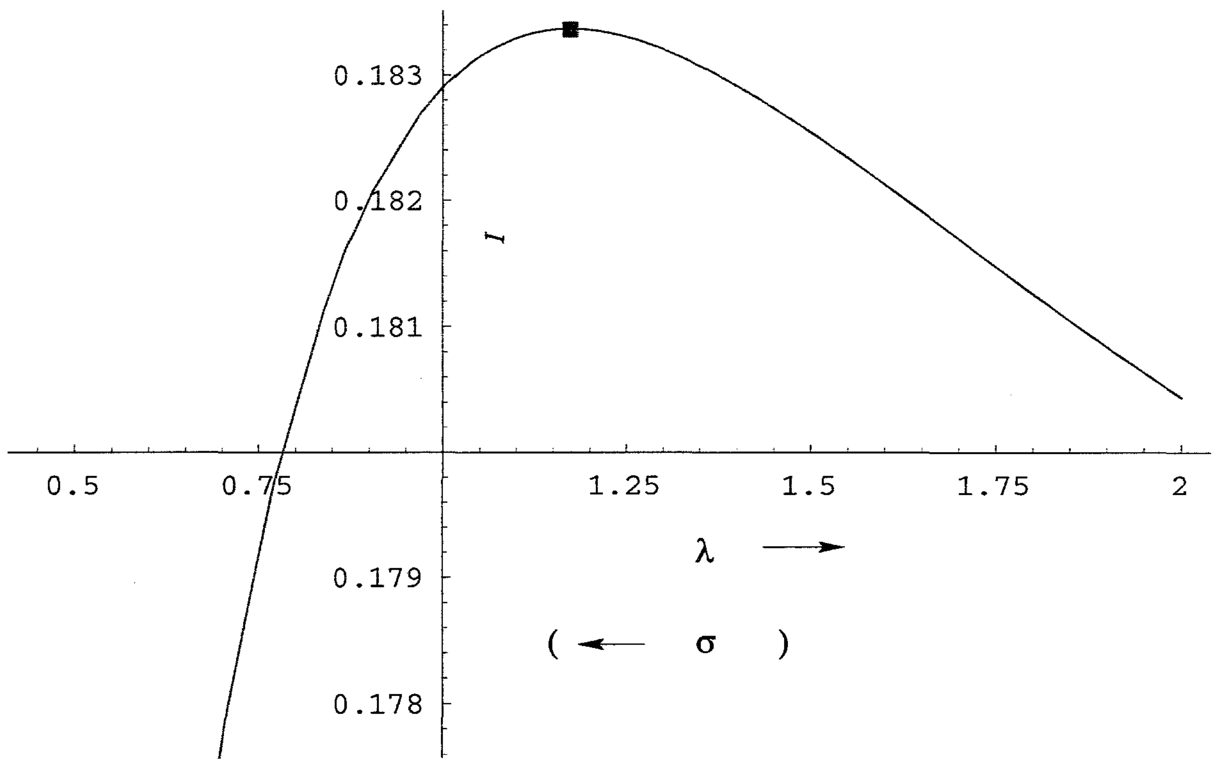
$\lambda = 0.5$ (stronger adsorption)



- A measure of interdigitation (overlap):

$$\begin{aligned} \mathcal{I}(\lambda) &= \int_0^\infty dz\, c_p(z,\lambda)\,[1 - c_p(z,\lambda)] \\ c_p(z,\lambda) &= \left[\frac{f_p(z,\lambda)}{f_p(z=0,\lambda)}\right]^2 \end{aligned} \tag{10}$$

- $\lambda_{optimal} \sim 1$, implying $\sigma_{optimal} \sim 0.02$, for PDMS.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